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Remarks: General

The claims have been amended by rewriting Claim 20; canceling Claims 24 and 26 without prejudice to or disclaimer of the subject matter thereof; and adding new Claims 27~31.   No new matter is added by these amendments.

New Claims 27~31 correspond, respectively, to original Claims 20, 21, 22, 23 and 25.

A petition under 37 CFR §1.136 for a three-month extension of time to respond the Examiner's action is enclosed, the fee for which should be charged to Deposit Account No. 04-1928 (E.I. du Pont de Nemours and Company).

By Applicant's calculation, no fees are due by reason of the addition of new Claims 27~31.   The cancellation of Claims 24 and 26 has been taken into account in the calculation of the fees.   If, however, Applicant's calculation is in error, or if any fee other than or in addition to those mentioned specifically above is required to authorize or obtain consideration of this response, please charge such fee to Deposit Account No. 04-1928.

Claims 20~23, 25 and 27~31 are now active in the application.   Applicant hereby requests reconsideration and further examination of the application in view of the reasons it has set forth below for allowance of the claims.

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Remarks: Detailed Action

I.

In Item 1, the Examiner has rejected Claims 20 and 22~26 under 35 U.S.C. §103(a) as being unpatentable over Regnier, *Phytochemistry,* Volume 6 (1967), Pages 1281~1289 in view of Mallat et al, *Applied Surface Science* 40 (1990), Pages 309~313.

Claim 21 remains pending in the application, but Claims 24 and 26 have been canceled, and Claims 27~31 have been added. A full copy of the Mallat reference is attached.

On pages 1284~1286, Regnier discloses for use in the hydrogenation of nepetalactone catalysts that may be platinum, platinum oxide or palladium on strontium carbonate. Regnier thus does not teach or suggest anything about the subject matter of Claims 20~23, 25 and 27~31 because those claims are directed to a process in which the hydrogenation occurs in the presence of palladium supported on a catalyst support that is not $SrCO_3$.

Mallat describes the effect of the phase structure of Pd-Cu catalysts, as resulting from the method of preparation of the catalyst, on the activity of the catalyst in a liquid phase hydrogenation. Mallat thus does not add anything to Regnier that would teach or suggest the subject matter of Claims 20~23, 25 and 27~31 because Mallat is concerned with the performance of a Pd-Cu catalyst whereas Claims 20~23 and 25 are directed to the use of a catalyst with a metal promoter that does not include copper, and Claims 27~31 are directed to the use of a catalyst that consists essentially of palladium supported on a catalyst that is not $SrCO_3$. The presence of the copper in the catalyst described by Mallat definitely has a material effect on the performance of the two metals together for catalytic purposes.

The field of catalysis is so unpredictable that it is not possible to infer from the use of a particular catalytic substance on a particular support that the same catalytic substance would perform the desired function on a different support, or that a different catalytic substance would perform the desired function on the same support. It is also not possible to infer from the use of a particular metal pair for catalytic purposes that a different metal pair, or that one metal in the absence of the other, would also perform the desired function.

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Regnier's disclosure of the use of a palladium on strontium carbonate catalyst thus does not teach or suggest anything about whether palladium on supports other than strontium carbonate would perform the desired catalytic function, as Applicant has discovered that it does. Moreover, Mallat's disclosure of use of the Pd-Cu pair in a hydrogenation does not teach or suggest anything about whether palladium would also perform the desired catalytic function in the presence of another metal, or in the absence of copper or another such metal.

In view of the distinctions between Regnier and Mallat, and the subject matter of Claims 20-23 and 25 as discussed above, Applicant respectfully requests that the Examiner withdraw the rejection of those claims under 35 U.S.C. §103(a). Applicant further submits that Claims 27-31 are also patentable for the same reasons.

In view of the foregoing, Applicant submits that all of the Examiner's objections and rejections have been properly traversed, and that the pending claims are in condition for allowance, request for which is hereby respectfully made.

Respectfully submitted,

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Appendix A

(i) Amendments
in marked-up form to
Claim 20,

(ii) New Claims 27~31, and

(iii) Status of all other claims

1~19. (canceled)

20. (currently amended) A process for the production of a dihydronepetalactone of formula (XVI) comprising hydrogenating a nepetalactone of formula (XV) according to the following scheme:

(XV)   (XVI)

in the presence of (a) palladium supported on a catalyst support that is not SrCO$_3$, and (b) a metal promoter selected from the group consisting of (i) those elements from groups 1 and 2 of the periodic table; (ii) tin, gold, silver and combinations thereof; and (iii) combinations of group 8 metals of the periodic table.

21. (original) The process as recited in Claim 20 wherein the catalyst support is selected from the group consisting of carbon, alumina, silica, silica-alumina, titania, titania-alumina, titania-silica, barium, calcium, compounds thereof, and combinations thereof.

22. (original) The process as recited in Claim 20 wherein the catalyst support is carbon.
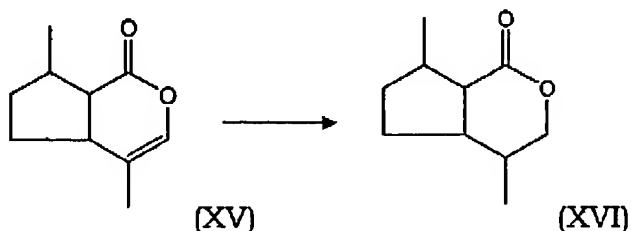
23. (previously presented) The process as recited in Claim 20 wherein the palladium content is from about 0.1 wt% to about 20 wt%.

24. (canceled)

25. (original) The process as recited in Claim 20 which is performed at a temperature of about 25°C to about 250°C and a pressure of about 0.1 MPa to about 20 MPa.

26. (canceled)

27. (new) A process for the production of a dihydronepetalactone of formula (XVI) comprising hydrogenating a nepetalactone of formula (XV) according to the following scheme:

(XV)   (XVI)

in the presence of a catalyst that consists essentially of palladium supported on a catalyst support that is not $SrCO_3$.

28. (new) The process as recited in Claim 27 wherein the catalyst support is selected from the group consisting of carbon, alumina, silica, silica-alumina, titania, titania-alumina, titania-silica, barium, calcium, compounds thereof, and combinations thereof.

29. (new) The process as recited in Claim 27 wherein the catalyst support is carbon.

30. (new) The process as recited in Claim 27 wherein the palladium content is from about 0.1 wt% to about 20 wt%.

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     31. (new) The process as recited in Claim 27 which is performed at a temperature of about 25°C to about 250°C and a pressure of about 0.1 MPa to about 20 MPa.

PHASE STRUCTURE OF CARBON SUPPORTED PALLADIUM–COPPER CATALYSTS

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The phase structure of 7%Pd–3%Cu on activated carbon catalysts was studied by potentiodynamic polarization and XRD methods. Unalloyed Pd, Pd-rich disordered alloy, unalloyed Cu and Cu_3Pd phases and adsorbed Cu have been detected, depending on the preparation methods. Activity in hydrogenation reactions was attributed to the Pd-rich disordered alloy phase.

1. Introduction

Pd–Cu catalysts have attracted attention from both theoretical and practical points of view. On the one hand, this couple is a typical representative of the thoroughly investigated VIII–IB alloys [1–3], on the other, copper has a beneficial effect on the selectivity of palladium in some partial hydrogenation reactions [4–8]. Nevertheless, the correlation between surface structure and catalytic features is still not clear.

It has been proved by XPS and AES measurements that heat treatment (500 K and above) in vacuum, hydrogen or air [9–12] caused a copper enrichment which is in accord with segregation theories [13–15]. In our opinion, however, the study of the copper-to-palladium ratio alone does not give enough information to answer the above question. Dowden [1] has pointed out that in such a complicated system as Pd + Cu, where more than two phases might be present on the surface, activity changes are not easy to understand unless

the special composition of the ensembles was recognized.

Palladium and copper form a homogeneous solid solution (fcc) in equilibrium up to 40 at% Cu [16]. Above this concentration Cu-rich disordered and ordered phases ($CuPd$ and Cu_3Pd) may be formed. Five different copper containing phases may be present on the surface of the catalyst, of which unalloyed copper is inactive in hydrogenation reactions below 100°C. Theoretically, the increased selectivity of Pd–Cu catalysts may be due to the presence of (i) Pd-rich disordered alloy, (ii) Cu-rich disordered alloy or (iii) Cu_3Pd phase. It is very probable that a CuPd ordered phase does not play any role in this study because it could be prepared only after special heat treatment [16].

This type of catalysts is used mainly in the liquid phase (e.g. hydrogenation, hydrogenolysis, oxidation) and the temperature of its preparation and application is generally below 400 K.

The aim of our study was to investigate the

effect of preparation methods on the phase structure of Pd–Cu catalysts supported on activated carbon. The phase structure of different Pd–Cu catalysts was studied electrochemically (by potentiodynamic sweeps) and by XRD. The applicability of potentiodynamic polarization for the determination of the phase structure of the Pd + Cu system has been proved on melted and homogenized sheets [17] and unsupported alloy-powders [18].

2. Experimental

Analytical grade reagents and distilled water were used.

The support was activated carbon (Carbo C Extra, BET surface area: 910 m^2 g^{-1}). Metal loadings were 7 wt% Pd and 3 wt% Cu in each case. The Pd- and Cu-containing salts were applied on the support by impregnation (incipient wetness method). The main parameters of catalyst preparation are gathered in table 1. After reduction the catalysts were washed with water (1000 × by weight) in hydrogen (to remove Cl^-), in argon and then in air and dried in vacuum, at room temperature.

The cell and electrochemical polarization method have been described before [17,19]. The potential of the catalyst was measured with respect to a hydrogen electrode immersed in the same supporting electrolyte which was in the main compartment of the cell.

Before the polarization 6 mg of dry catalyst powder was put on the smooth platinum sheet electrode. The cell was purged with N_2 for 1 h,

with H_2 for 2 h and then filled with 0.5M H_2SO_4 supporting electrolyte saturated with H_2. Hydrogen was bubbled through the cell for 1 h to complete the reduction of the sample, then excess H_2 was flushed out of the cell by de-oxygenated N_2. Anodic polarization commenced from 0.03 V with a sweep rate of 10 mV min^{-1}.

The sulfuric acid electrolyte was prepared from triply distilled water and Merck analytical grade reagent.

The lattice parameters were measured by Philips PW 1050 high angle X-ray powder diffractometer ($K_{\bar{a}}$ = 154.18 pm, scanning speed: 1° (2θ) min^{-1}).

The activity of the catalysts was measured in the liquid phase hydrogenation of hexen-1-one-5 (to hexanone-2), nitrobenzene (to aniline) or acetophenone (to 1-phenyl-ethanol and ethylbenzene). 1 cm^3 of reagent in 9 cm^3 of ethanol was reduced with 50 mg of catalyst at 23–25°C and 1 bar (n = 900 min^{-1}). Initial rates were determined by extrapolating the hydrogen consumption to zero time.

3. Results and discussion

The 7%Pd–3%Cu/C catalysts were prepared by usual, conventional methods. The parameters and precursors were varied, but organic materials (as solvent, precursor or reducing agent) were excluded, because of possible surface contaminations.

The potentiodynamic polarization curves of the catalysts prepared by simultaneous reduction are shown in fig. 1. It has been proved on unsupported powders that Cu dissolution in Pd (dis-

Table 1
Preparation of carbon supported Pd–Cu catalysts

Catalyst	Method of impregnation	Precursors	Reducing agents	Temp. (°C)	Time of reduction (h)
A	Simultaneous	/Pd(NH$_3$)$_4$/(OH)$_2$ + /Cu(NH$_3$)$_4$/(OH)$_2$	H$_2$	200	1
B	Simultaneous	K$_2$PdCl$_4$ + CuCl$_2$	H$_2$	80	0.5
C	Simultaneous	K$_2$PdCl$_4$ + CuCl$_2$	NaBH$_4$	25	0.3
D	Simultaneous	PdO·xH$_2$O + Cu(OH)$_2$	H$_2$	25	6
E	Consecutive	K$_2$PdCl$_4$ + CuCl$_2$	H$_2$	25	1
F	Consecutive	K$_2$PdCl$_4$ + /Cu(NH$_3$)$_4$/(OH)$_2$	H$_2$	25	1
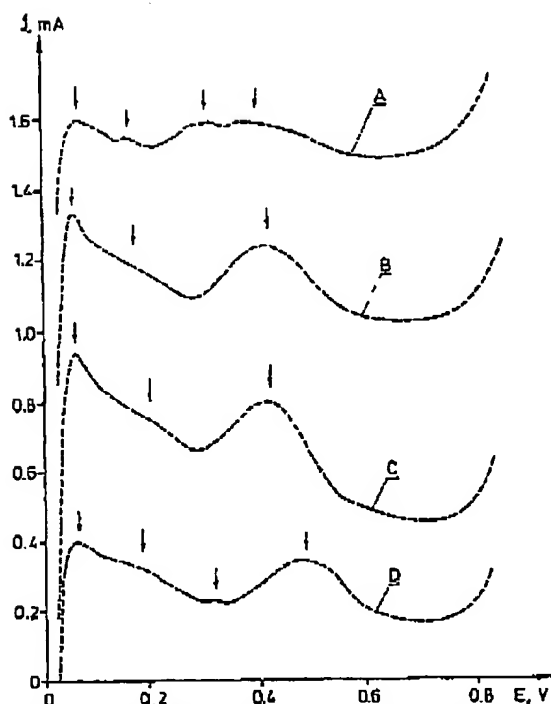
Fig. 1. Potentiodynamic polarization curves of catalysts A–D, prepared by simultaneous reduction.

solution of unalloyed Cu (0.3–0.4 V) and the Cu$_3$Pd phase (0.5–0.6 V) are partly separated or not separated at all. The overlapping of the peaks may be connected with the dependence of the ionization potential on the dispersity, crystallographic surface structure and topography of the metal catalyst. For example, the potential of the peak maximum of the dissolution of the Cu$_3$Pd phase was about 0.5 V on carbon supported Pd–Cu catalysts, about 0.1 V lower than on unsupported alloy powders [22]. It may be concluded from the shape of the curves and from the potentials of the beginning of dissolution that catalyst A contains the largest amount of unalloyed Cu, whereas the amount of Cu phase is negligible in catalyst D.

Cu$_3$Pd phase and unalloyed Cu (in catalysts B and D) could not be detected by XRD (table 2). The explanation may be that the size of this phase was too small ("X-ray amorphous") and/or it was present in a non-crystalline form. It was found earlier [17] that the diffractograms show the presence of Cu$_3$Pd in alloy sheets only after a 100 h thermal treatment at 400 °C.

The voltammograms of catalysts E and F, prepared by consecutive reduction of Cu^{2+} onto the surface of carbon supported Pd, are seen in fig. 2. The characteristic surface phase is unalloyed Cu in both cases. (The interpretation of the doublet at 0.3–0.4 V can be found elsewhere [23].) The increased current between 0.4–0.6 V may correspond to the ionization of either a Cu$_3$Pd phase or adsorbed Cu [23–25]. It is not simple to distinguish them, as the potential range of their dissolution is about the same. In general, metal adsorption is a typical surface phenomenon, but the "two-dimensional" alloy may turn after some time

ordered alloy) decreases the peak potential of both absorbed (weakly bound) and adsorbed (strongly bound) hydrogen [20]. Unfortunately, the two main types of hydrogen are hardly distinguishable on the voltammograms of carbon supported catalysts. This may be caused in part by the carbon support [21], and in part by the presence of various alloy phases with copper contents of a broad composition range. The latter statement is supported by the results of XRD study of the bulk structures (table 2). The peaks of the Pd-rich alloy phase in the diffractograms have trapezoidal maxima, covering a broad concentration range. (The approximate Cu content of the alloy phase was calculated from the known correlation between lattice constant and bulk composition [20].)

The interpretation of the voltammograms in the range of metal dissolution (0.3–0.7 V) is much more difficult than it was in the case of unsupported alloy powders [18]. The peaks of the dis-

Table 2
Phases detected by XRD

Catalyst	Phases (Cu content in at%)
A	Alloy (0–20), Cu
B	Alloy (0–40)
C	Alloy (0–20), Cu
D	Alloy (0–40)
E	Pd, Cu
F	Pd, Cu

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to a real, bulk alloy, for which there are several examples [26]. To check this possibility we extended the reduction step of the catalyst preparation for more than 200 h, but no change could be detected, thus, the formation of Cu_3Pd can be excluded.

There are considerable hydrogen ionization peaks around 0.1 V (fig. 2), which are believed to be the distorted ionization maxima of hydrogen, dissolved in the unalloyed, bulk Pd.

The catalysed reduction of Cu^{2+} at the surface of Pd metal results in a cherry-type alloy. Unalloyed, bulk Pd (see XRD data, table 2) is covered by bulk Cu and some adsorbed Cu. Unalloyed Cu behaves as a barrier in the oxidation process of absorbed hydrogen.

The absence of active sites for hydrogen adsorption (and thus for hydrogenation reactions) is proved by catalytic investigations (table 3). Initial reaction rates were measured in the liquid phase hydrogenation of organic molecules with $>C=C<$, $>C=O$ or $-NO_2$ functions. The activities of catalysts E and F are about two orders lower than those of catalysts prepared by simultaneous reduction.

From catalytic aspects the most interesting question is the relation between catalytic activity and (surface) phase structure. To answer this question it is necessary to know which of the
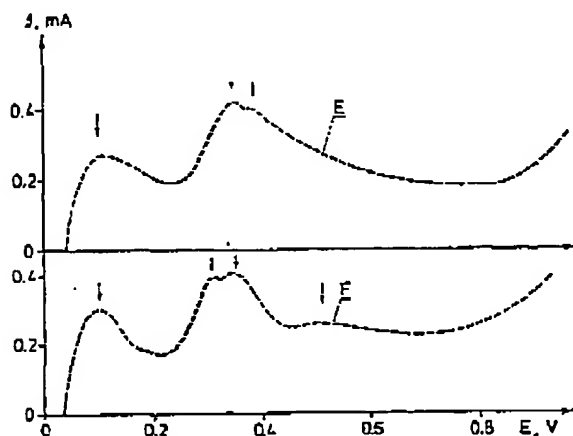
Table 3
Activities of Pd–Cu/C catalysts in liquid phase hydrogenation

Catalyst	Activities, mol h^{-1} (g catalyst)$^{-1}$		
	Hexen-1-one-5	Nitrobenzene	Acetophenone
A	6.4	2.0	0.02
B	33	9.4	1.4
C	42	18	3.3
D	21	6.9	3.0
E	0.75	0.15	0.01
F	1.4	0.20	0.01

phases are active (the nature of active sites) and to know the specific surface area of the phases. As to the former, it is certain that the Pd-rich disordered alloy (and the Pd itself) are active in hydrogen sorption, while unalloyed (bulk) Cu and adsorbed Cu are inactive at room temperature. It is likely that the Cu_3Pd phase behaves similarly to adsorbed Cu, as the energies of Pd–Cu bonds are similar. Nevertheless, for an unambiguous evidence one should prepare a catalyst with only Cu_3Pd phase on its surface (without Pd-rich alloy). Unfortunately, this has not been succeeded yet. We tried to reproduce the result of the only reference [27] in the literature of preparing Cu_3Pd powder, but the product was far from being uniform [17].

To our knowledge there is no reliable method for measuring the specific active surface area of Pd–Cu catalysts. As an approximation we used hydrogen sorption and X-ray line broadening. The amount of sorbed hydrogen was calculated from the area under the polarization curves (fig. 1). The shortcomings of the method are: (i) the Me/H_{ads} ratio is considered to be 1.0, though it should depend on Cu content, (ii) there is still some dissolved hydrogen, which disappears only above 40 at% Cu content [20] or at high dispersity [28], (iii) the hydrogen adsorbed on the carbon support of high surface area is not negligible.

An approximate particle size was calculated from the X-ray line broadening of the Pd-rich disordered alloy phase (hkl: 111). The problem was that the presence of alloy phases with various Cu contents caused an increase in half-width, too.

Because of the uncertainties discussed above we considered only the sequence of catalysts A–D

Fig. 2. Potentiodynamic polarization curves of catalysts E and F, prepared by consecutive reduction.

according to the number of active sites:

C > B > D ~ A

(from X-ray line broadening), and

C > B > D > A

(from hydrogen sorption). This is in astonishingly good correlation with the sequence of activities (table 3):

C > B > D > A.

Excluding chance coincidence, the excellent correlation concerning some simple hydrogenation reactions can be explained by the similarity in surface phase structure of the catalysts prepared by various simultaneous reduction methods. It follows that surface Cu and Cu_3Pd phases (fig. 1) behave similarly – both are inactive at 25°C and 1 bar. Naturally, this assumption needs further evidence.

4. Summary

The phase structure of the 7%Pd–3%Cu/C catalysts prepared by consecutive reduction resembles the so-called cherry-model: unalloyed Pd is covered by unalloyed Cu and some adsorbed Cu.

The catalysts prepared by simultaneous reduction contained Pd-rich disordered alloy, unalloyed Cu and an intermetallic compound phase (Cu_3Pd). The presence of the latter could not be proved in the bulk by XRD. The ratio of the phases on the surface depended on the preparation method, but all three phases were present in every case.

Acknowledgements

References

[1] D.A. Dowden, in: Proc. 5th Intern. Congr. on Catalysis, Miami, 1972 (North-Holland, Amsterdam, 1973) p. 621.
[2] G.C. Bond, Catalysis by Metals (Academic Press, New York, 1962).
[3] J.K.A. Clarke, Chem. Rev. 75 (1975) 291.
[4] N.V. Bizhanova, M.S. Erzhanova and D.V. Sokolskii, Izv. Akad. Nauk Kaz. SSR Ser. Khim. 19 (1949) 15.
[5] P.V. Mokroushav and A.I. Naumov, in: Catalytic Reactions in the Liquid Phase, Tr. Vses. Konf. Alma-Ata, Kaz. SSR, 1966 (1967) p. 10 (in Russian).
[6] British patent 1,510,195 (1978); US patent 4,021,374 (1977).
[7] German patent 2,506,157 (1977).
[8] L. Guczi, Z. Schay, A.H. Weiss, V. Nair and S. Le Viness, Reaction Kinet. Catalysis Letters 27 (1985) 147.
[9] E.S. Shpiro, T.S. Ustinova, V.S. Smirnov, V.M. Gryaznov, G.V. Antoshin and H.M. Minachev, Izv. Akad. Nauk SSSR Ser. Khim. (1978) 763.
[10] A.D. van Langeveld, H.A.C.N. Hendricks and B.E. Nieuwenhuys, Thin Solid Films 109 (1983) 179.
[11] T.S. Sampath Kumar and M.S. Hegde, Appl. Surface Sci. 20 (1985) 290.
[12] D.C. Peacock, Appl. Surface Sci. 27 (1986) 58.
[13] V. Ponec, Catalysis Rev.-Sci. Eng. 11 (1975) 41.
[14] V. Ponec, Surface Sci. 80 (1979) 352.
[15] M. Kelley, J. Catalysis 57 (1979) 113.
[16] M. Hansen, Constitution of Binary Alloys (McGraw-Hill, New York, 1958) p. 612.
[17] J. Petró, T. Mallát, S. Szabó and F. Hange, J. Electroanal. Chem. 160 (1984) 289.
[18] T. Mallát and J. Petró, J. Electroanal. Chem. 239 (1988) 409.
[19] S. Szabó, J. Electroanal. Chem. 77 (1977) 193.
[20] T. Mallát and J. Petró, Acta Chim. Hung. 108 (1981) 381.
[21] É. Polyánszky, T. Mallát and J. Petró, Acta Chim. Hung. 92 (1977) 147.
[22] T. Mallát, J. Petró and M. Schäffer, Acta Chim. Hung. 98 (1978) 175.
[23] S. Szabó, I. Bakos, F. Nagy and T. Mallát, J. Electroanal. Chem. 263 (1989) 137.
[24] R.R. Adžić, M.D. Spasgević and A.R. Respič, J. Electroanal. Chem. 92 (1978) 31.
[25] T. Chierchie and C. Mayer, Electrochim. Acta 33 (1988) 344.
[26] D.M. Kolb, Advan. Electrochem. Eng. 11 (1978) 125.
[27] S.M. Kulifay, J. Am. Chem. Soc. 83 (1961) 4916.
[28] W. Paleewska, in: Hydrogen Effects in Catalysis, Eds. Z. Paál and P.G. Menon (Dekker, New York, 1988) p. 373.